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(54) **Printing paper and method of image formation employing the same.**

(57) A printing paper is provided which is a neutralized paper comprising a cationic compound on the printing surface of base paper and having a surface pH value ranging from 6.0 to 7.5.

**EP 0 652 113 A1**

## BACKGROUND OF THE INVENTION

### Field of the Invention

The present invention relates to a printing paper which is based on neutralized paper and exhibits excellent performance as toner-transfer paper for electrophotographic printing, and also relates to a method of image formation by electrophotographic printing by use of this printing paper.

The present invention further relates a printing paper which is based on neutralized paper and capable of forming sharp images in ink-jet recording, and also relates to a method of image formation by ink-jet printing by use of this printing paper.

### Related Background Art

An electrophotographic copying machine is exemplified by a copying machine which conducts printing through the process of: charging a photoconductive photosensitive member by means of a temporary electric charger; exposing the photosensitive member to light to form a latent image; developing the latent image with a developing toner of one- or two-component type, transferring the toner image from the photosensitive member to a printing paper sheet fed from the outside by means of a toner-transfer electric charger, and fixing the transferred toner on the printing paper sheet by action of heat and/or pressure by means of a fixing roller or the like to obtain a final copied image.

The properties required for the transfer paper for such a copying machine are as follows:

- (1) optimum surface electrical resistance and optimum surface smoothness and good in satisfactory toner transfer property,
- (2) excellent in toner-fixing properties,
- (3) less paper dust formation, i.e., causing no image defect by sticking of the formed paper dust on a photosensitive member, an electric charging roller, etc.,
- (4) causing no scrape nor abrasion of the photosensitive member, the paper-delivering roller, fixing rolls, etc. by the formed dust (filler, etc.),
- (5) generating no curling by action of heat,
- (6) generating no variation of the paper dimension by humidity change,
- (7) low stiffness, and optimum surface friction coefficient and excellent in deliverability.

In recent years, neutralized paper has come to be used widely in place of conventional acidic paper for storability of paper and other reasons. Japanese Patent Application Laid-open No. 59-191068 discloses toner-transfer paper suitable for electrophotographic printing.

On the other hand, the ink-jet printing system is attracting attention because of ease of high speed printing, color printing, and high-density printing, and therefore the ink-jet printing apparatus has come to be used widely. In particular, for mono-color printing and business color printing, the ink-jet printing is required to be suitable for printing on inexpensive ordinary paper which is available in offices, not on ink-jet printing paper exclusively used.

No toner-transfer paper is presently known which is suitable also for ink-jet printing.

When the toner-transfer paper, which is neutralized paper, is used for ink-jet printing, disadvantages are involved such as insufficient ink-fixing properties, insufficient water fastness of the printed image owing to water-soluble printing agent, insufficient coloring ability of the coloring agent.

## SUMMARY OF THE INVENTION

The present invention intends to provide a printing paper which comprises neutralized paper as the base material and satisfies the requirements for a toner-transfer paper for electrophotographic printing, in particular, having excellent toner fixation properties, and is also useful for ink-jet printing without the above-mentioned disadvantages.

The present invention also intends to provide a method for forming an image on the aforementioned printing paper by electrophotographic printing as well as by ink-jet printing.

The object mentioned above can be achieved by the present invention.

According to the present invention, there is provided the printing paper which is neutralized paper comprising a cationic compound on a printing surface of base paper, and having a surface pH value ranging from 6.0 to 7.5. The printing paper is coated with a material containing a substance which lowers the surface pH value of the base paper, and has a Stoeckigt sizing degree ranging from 16 to 40 seconds.

According to the present invention, there is also provided the image-forming method comprising steps of developing an electrostatic image by a developing means with a toner, transferring a toner image developed on a photosensitive member onto a transfer-receiving material by a transfer means, and fixing the image formed on the transfer-receiving material by heat and/or pressure with a pair of rollers to form a fixed image, the transfer-receiving material being the above-defined printing paper.

According to the present invention, there is further provided the image-forming method which is an ink-jet printing method to conduct printing by applying an ink comprising a dye, a low-boiling solvent, a non-volatile solvent, and a nitrogen-containing compound to the above-defined printing paper.

## 10 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates an example of printing means of electrophotographic copying machines.

Fig. 2 illustrates an example of fixation devices of electrophotographic copying machines.

## 15 DESCRIPTION OF THE PREFERRED EMBODIMENTS

After comprehensive studies, it has been found by the inventors of the present invention that toner-transfer paper based on neutralized paper has excellent electrophotographic printing characteristics, in particular, excellent toner fixing properties, and yet has excellent ink-jet printing characteristics such as sufficient ink-fixing properties with high water-fastness of the printed image and sufficient coloring ability of a coloring agent, by applying a cationic resin on a surface by means of a size press coating and adjusting a surface pH value within a specified range.

The printing paper employed in the present invention is made by a conventional paper-making process from chemical pulp represented by LBKP, NBKP, etc., a sizing agent, and a filler as the main components and additionally necessary paper-making auxiliary agents. The pulp may be mechanical pulp, a regenerated waste paper, or combination thereof.

The sizing agent includes rosin sizes, alkyl ketene dimers, alkenylsuccinic anhydrides, petroleum resin sizes, epichlorohydrin, acrylamide, etc.

The filler includes calcium carbonate, kaolin, talc, titanium dioxide, etc.

In producing the printing paper of the present invention, the pulp slurry prepared by dispersing the above materials is adjusted to have a pH of about 7 or higher, due to no use of aluminum sulfate as a fixing agent for the sizing agent, or the use thereof as less as possible.

The printing paper of the present invention is obtained by treating the above-produced paper for size press coating as usual with starch or the like in order to improve the surface strength and writing quality of the paper.

The surface pH value of the printing paper is adjusted finally by the aforementioned size press coating in the present invention. The sizepress coating solution contains preferably a substance for lowering the surface pH value of the base paper, more preferably a cationic compound, to adjust the pH within the above-mentioned range.

The cationic compound in the present invention means a compound which has, in the main chain or the side chain thereof, a functional group such as primary, secondary, and tertiary amino, quaternary ammonium, pyridyl, pyridinium, imidazolyl, imidazolinium, sulfonium, phosphonium, and the like, preferably strong acid salts thereof. Such cationic compounds include homopolymers of cationic vinyl compounds such as polyvinylamine, polyallylamine, polydiallylamine, polydimethylaminoethyl methacrylate and salts thereof; and cation-modified polyvinyl alcohol, polyvinylpyrrolidone, polyacrylamide, etc. modified by partially copolymerizing the above functional vinyl monomer with another vinyl monomer; cationized hydroxyethyl-cellulose, and cationized starch.

The properties of printing paper of the present invention are controlled as follows.

The surface electric resistance is in the range of from  $10^9$  to  $10^{12} \Omega$ . The surface electric resistance outside this range causes incomplete toner transfer, toner stains on white portions of the print, so called fogging.

In view of the paper deliverability and the curling tendency, the paper is controlled to have basis weight in the range of from 60 to 90 g/m<sup>2</sup>, a density of the paper in the range of from 0.6 to 0.8 g/m<sup>3</sup>, a water content of the wet web in paper-making in the range of from 3.5 to 7% by weight, the stiffness in the range of from 50 to 130 cm<sup>3</sup>/100 in the MD direction, and from 25 to 100 cm<sup>3</sup>/100 in the CD direction.

The whiteness degree of the paper is not lower than 75 %, and the opacity thereof is not lower than 80 %.

The surface electric resistance is measured according to JIS-C-2111 (20°C/65%RH), the basis weight according to JIS-P-8124, the density according to JIS-P-8118, the water content according to JIS-P-8127, the stiffness according to JIS-P-8143, the whiteness degree according to JIS-P-8123, and the opacity according to JIS-P-8138.

The Stoeckigt sizing degree of the printing paper of the present invention is preferably in the range of from 16 to 40 seconds. When the printing paper of the Stoeckigt sizing degree of lower than 16 seconds is used for ink-jet printing, the ink is liable to run on the paper surface, and feathering of the printed dots and broadening of printed lines are liable to occur, impairing the printed character quality. On the other hand, with the printing paper of the Stoeckigt sizing degree of higher than 40 seconds, ink absorbency is not sufficient to require a long time for drying of the ink at the printed portion, and the printed image quality is liable to be impaired by smearing before drying of the ink.

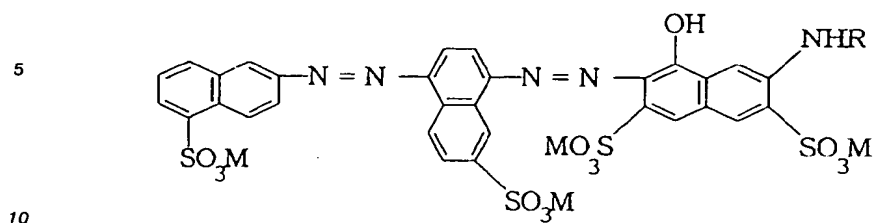
Fig. 1 illustrates an example of the printing means of an electrophotographic copying machine. A photoconductive photosensitive member 3 is electrically charged by means of a temporary electric charger 5. Then the charged sensitive member is exposed to light imagewise to form a latent image. The latent image is developed with a one- or two-component type toner 8 which is held in a developer 6 as the developing means to form a toner image. The toner image on the photosensitive member is transferred onto a printing paper sheet 4 fed from the outside, with a transfer charger 7 as the transfer means. Then, the toner image on the printing paper 4 is fixed by heat and/or pressure with a fixing device 13 as the toner device as shown in Fig. 2 which has a pair of rollers 9 and 10 (or one roller with one belt). Thus the final copied image is obtained. In the transfer process, unfixed toner and paper dust formed from the printing paper sheet 4 are removed to clean the photosensitive member 3 by a cleaner device 1 placed after the transfer step. After the cleaning with a cleaning member 2 (e.g., a cleaning blade) in contact with the photosensitive member 3, the surface of the photosensitive member is repeatedly subjected to the steps of charging, etc. In the fixing device 13, as shown in Fig. 2, the unfixed toner and the paper dust from the transfer paper 4 on the fixation roller 9 are removed with the cleaning member 11 brought into contact therewith and simultaneously a releasing agent such as silicone oil is applied to the roller.

Next, the ink-jet printing system is described below. In the ink-jet printing system, ink is effectively ejected from a nozzle onto a printing paper placed at a distance within the ink-shooting range. A typical example is disclosed in Japanese Patent Application Laid-open No. 54-59936, in which ink receives thermal energy to change its volume abruptly by bubbling and the change of the state gives driving force to eject the ink from the nozzle.

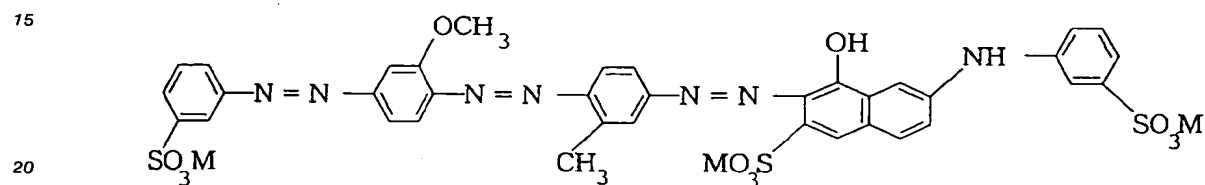
The ink employed for the ink-jet printing contains as the printing agent a water-soluble dye, e.g., direct dyes, acid dyes, basic dyes, reactive dyes, and food colors, etc., a disperse dye, a pigment, or the like. Of these, acid dyes and the direct dyes are widely used. Such a printing agent is contained in the ink in an amount of from about 0.1 to about 20 % by weight of the ink. The solvent for the ink is usually water or a mixed solvent of water with a water-soluble organic solvent. Particularly preferred solvents are mixed solvents composed of water and water-soluble organic solvents, containing a polyhydric alcohol and the like which are effective for prevention of drying of the ink. The ink which contains an acid dye or a direct dye usually contains as the dissolution aid for the dye a nitrogen compound such as ammonia (ammonium ion), urea or its derivative, an aminoalcohol, an alkylamine, and an amino acid.

The printing paper of the present invention has suitability for mono-color types of ink-jet printing. It is particularly suitable for printing system employing the ink which contains the black dye shown below and a nitrogen-containing compound as a dissolution aid.

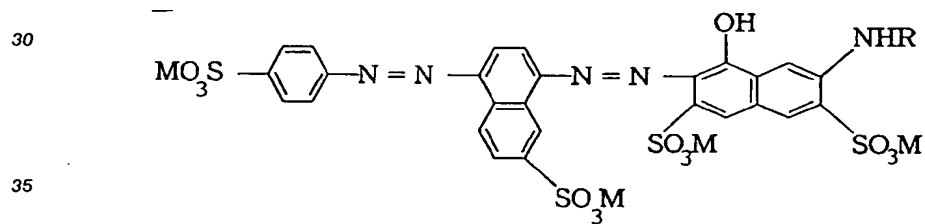
(1)



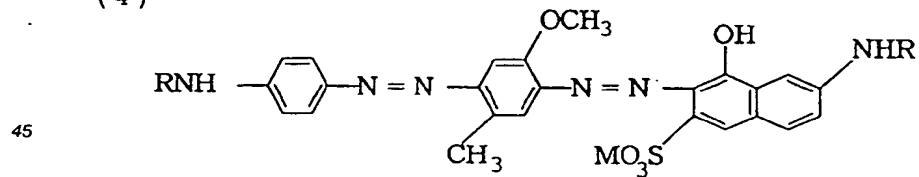
(2)



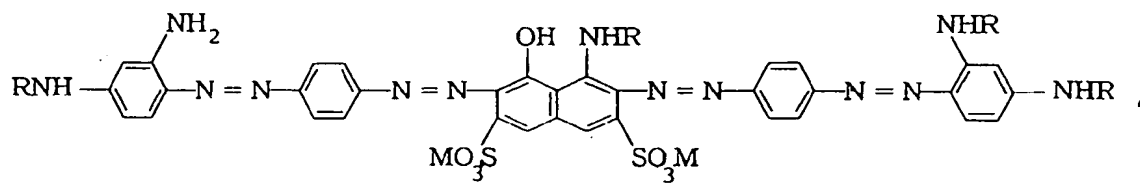
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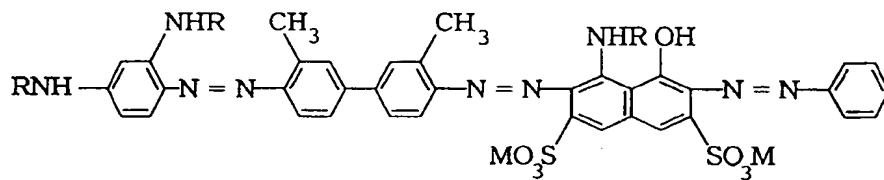
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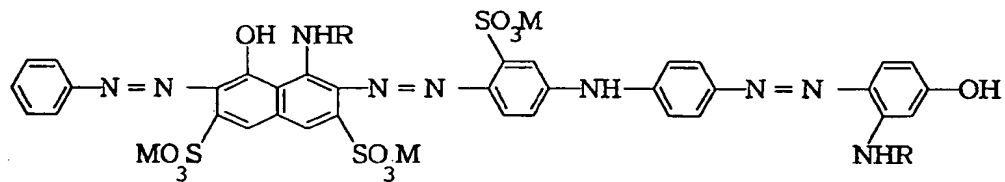
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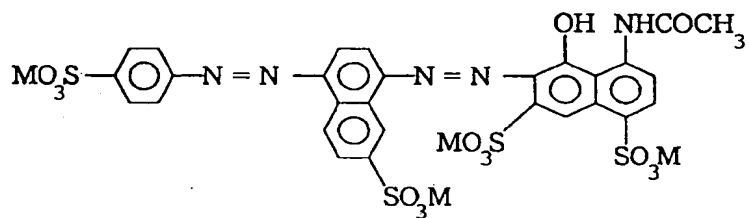
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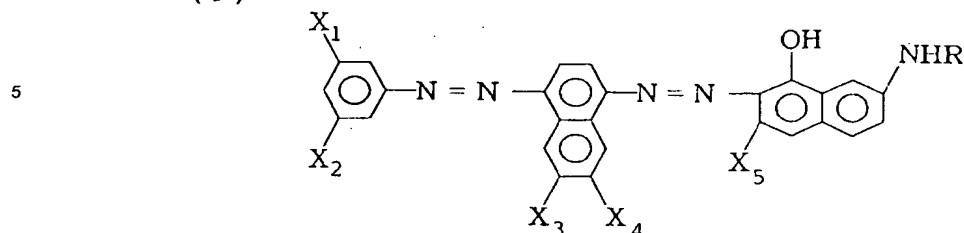


( 8 )



and

(9)



In the formulas, M is Na or Li; R is H or alkyl;  $X_1$  to  $X_5$  are independently H,  $\text{SO}_3\text{Y}_1$  or  $\text{COOY}_2$ ,  $\text{Y}_1$  and  $\text{Y}_2$  are independently Na, Li, K, or  $\text{NH}_4$ .

The present invention is described in more detail by reference to examples. In the following, "part" or "parts" is by weight unless otherwise noted.

#### [ Preparation of Printing Paper (1) ]

A mixture of 90 parts of LBKP and 10 parts of NBKP was used as the pulp material. The mixture was subjected to beating treatment. Thereto were added calcium carbonate, (Escalon, produced by Sankyo Seifun K.K.) as the filler, and an alkylketene dimer and a cationic starch as additives. The mixture was subjected to paper-making in a conventional manner to obtain a base paper sheet having a basis weight of 64 g/m<sup>2</sup> and Stoeckigt sizing degree of 18 seconds. To the base paper sheet, 2% oxidized starch aqueous solution was applied as the coating solution by means of a size press coating to obtain Printing Paper Sheet 1. Further, Printing Paper Sheets 2 through 4 were prepared from sizepress coating solutions having each composition mentioned below by size press. The surface pH values of the Printing Paper Sheets are shown in Table 1.

#### [ Preparation of Printing Paper (2) ]

A base paper sheet for printing was prepared in the same manner as above except that kaolin is used as the filler and neutral rosin size (Sizepine NT, produced by Arakawa Kagaku K.K.) was used in place of the alkylketene dimer. The base paper sheet had a basis weight of 67 g/m<sup>2</sup>, and the Stoeckigt sizing degree of 16 seconds. On the base paper sheet, the same coating solution as the one for Printing Paper Sheet 1 was applied to obtain Printing Paper Sheet 5. Further by application of the sizepress coating solution having composition below by a size press coating, Printing Paper Sheets 6 through 8 were obtained. The surface pH values of the respective paper sheets are shown in Table 1.

Composition of Sizepress Coating Solution for Printing Paper Sheets 2 to 4	
Oxidized starch (MS-3800, produced by Nippon Shokuhin K.K.)	2 parts
Polyamine sulfone (PAS-H, 10L produced by Nittobo K.K.)	X parts
Water	98-X parts
Printing Paper Sheet 2: X = 0.06	
Printing Paper Sheet 3: X = 0.2	
Printing Paper Sheet 4: X = 1.5	

Composition of Sizepress Coating Solution for Printing Paper Sheets 6 to 8	
Oxidized starch (MS-3800, produced by Nippon Shokuhin K.K.)	2 parts
Polyallylamine hydrochloride (PAAHCL, 10L produced by Nittobo K.K.)	X parts
Water	98-X parts
Printing Paper Sheet 6: X = 0.04	
Printing Paper Sheet 7: X = 0.1	
Printing Paper Sheet 8: X = 1	

#### [ Evaluation of Electrophotographic Printing Suitability ]

The suitability for electrophotographic printing was evaluated with the copied image quality formed by use of Copying Machine NP-9800, and Color Copying Machine CLC-500 (respectively trade names, manufactured by Canon K.K.) having an image forming device and a fixing device as shown in Figs. 1 and 2. The evaluation results are shown in Table 1 on three grades:

- a : Good (good at color tone, color reproducibility, and coloration);
- b : Fair; and
- c : Poor (dull coloration, blank portions found).

#### [ Evaluation of Ink-Jet Printing Suitability ]

The suitability for ink-jet printing was evaluated by printing with the inks below by means of an ink-jet printing apparatus having an ink-jet printing head comprising 14 printing nozzles per mm to eject ink droplets by action of thermal energy. The ink used and the evaluation items are shown below:

Ink Composition	
Dye	3 parts
Glycerol	6 parts
Ethanol	6 parts
Urea	6 parts
Water	79 parts

Ink I: The previously mentioned exemplified dye of Formula (9) was used (in the formula,  $X_1$  is 5-COONH<sub>4</sub>;  $X_2$  is 3-COONH<sub>4</sub>;  $X_3$  and  $X_4$  are H; R and  $X_5$  are H).

Ink II: A mixture (mixing ratio 1:1) of the previously mentioned exemplified dyes of Formula (1) and Formula (2) was used (in the formulas, M is Li; and R is H).

#### [ Evaluation Items ]

##### (1) Image density:

A black solid print image is formed by use of the aforementioned printing apparatus, and the density of the solid printing is measured by a MacBeth densitometer (RD-918).

##### (2) Water fastness:

Printing is conducted by use of the aforementioned printing apparatus. One hour after the printing, the printed matter is immersed in city water for 3 seconds and is dried spontaneously. After the drying, the water fastness is evaluated on four grades:

- A : No change of image observed;
- B : No change observed in printed area, slight tailing to non-printed area observed (re-adhesion of released dye);
- C : Printed area blurred, tailing to non-printed area significant; and
- X : Printed characters not decipherable.



## EP 0 652 113 A1

### (3) Black color tone:

- A : Printed area being recognized as black in the same area as the measurement of the image density;
- 5 B : Medium (poorer than A but better than C); and
- X : Printed area being recognized as dark brown.

### (4) Character quality:

- 10 A : Printed characters "a, b, c" in size of 3 × 3 mm having sharp edge; and
- X : Above printed characters having unclear edge, or undecipherable.

### (5) Rub fastness:

- 15 The printed matter, 15 seconds after printing, is rubbed with Silbon C paper (trade name) with load of 40 gf/cm<sup>2</sup>.
- A : No smearing observed; and
- X : Smearing observed.

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Table 1

Print- ing paper No.	Surface pH	Sizing degree (sec)	EPG *	Ink-jet recording suitability								Over- all eval- uation	Note **
				Ink I				Ink II					
				Image den- sity	Water fast- ness	Color tone	Char- acter qual- ity	Rub fast- ness	Image den- sity	Water fast- ness	Color tone		
1	8.6	18	c	1.38	C	X	A	A	1.34	X	X	Poor	CE-1
2	7.3	18	b	1.42	B	B	A	A	1.38	C	B	Good	E-1
3	6.5	18	a	1.43	B	A	A	A	1.33	C	A	Good	E-2
4	4.6	18	a	1.22	B	X	A	A	1.18	C	B	Poor	CE-2
5	8.0	16	c	1.41	C	B	A	A	1.37	X	A	Poor	CE-3
6	7.2	16	a	1.41	B	A	A	A	1.36	B	A	Good	E-3
7	6.2	16	a	1.39	A	A	A	A	1.33	B	A	Good	E-4
8	3.6	16	a	1.26	A	X	A	A	1.21	B	X	Poor	CE-4

\* Electrophotographic printing suitability

\*\* E- : Example No., CE-: Comparative Example No.

The printing paper of the present invention is neutralized paper formed to have the aforementioned excellent properties and to be suitable for electrophotographic copying, further having a surface pH value adjusted to 6.0 to 7.5 by sizepress coating containing a strong acid salt of a cationic compound. Such toner-transfer paper satisfies the various electrophotographic printing suitability and excellent in toner fixing properties, and paper deliverability.

Furthermore, the printing paper of the present invention is excellent in printing suitability also for ink-jet printing with a mono- or multi-color, exhibiting excellent coloring properties of the printing agent, and giving images with sufficient density and black tone. In particular, the printing paper of the present invention is satisfactory in comparison with conventional neutralized paper having higher surface pH which is insufficient in water-fastness of image and black tone of images.

A printing paper is provided which is a neutralized paper comprising a cationic compound on the printing surface of base paper and having a surface pH value ranging from 6.0 to 7.5.

#### Claims

1. A printing paper which is a neutralized paper comprising a cationic compound on a printing surface of base paper, and having a surface pH value ranging from 6.0 to 7.5.
2. The printing paper according to claim 1 wherein the surface of the base paper is coated with a material containing a substance which lowers the surface pH value of the base paper.
3. The printing paper according to claim 1, wherein a Stoeckigt sizing degree is ranging from 16 seconds to 40 seconds.
4. An image-forming method comprising steps of developing an electrostatic image by a developing means with a toner, transferring a toner image developed on a photosensitive member onto a transfer-receiving material by a transfer means, and fixing the image formed on the transfer-receiving material by heat and/or pressure with a pair of rollers to form a fixed image, said transfer-receiving material being the printing paper as defined in any one of claims 1 to 3.
5. An image forming method, which is an ink-jet printing method to conduct printing by applying an ink comprising a dye, a low-boiling solvent, a non-volatile solvent, and a nitrogen-containing compound to a printing paper, said printing paper is as defined in any one of claims 1 to 3.

FIG.1

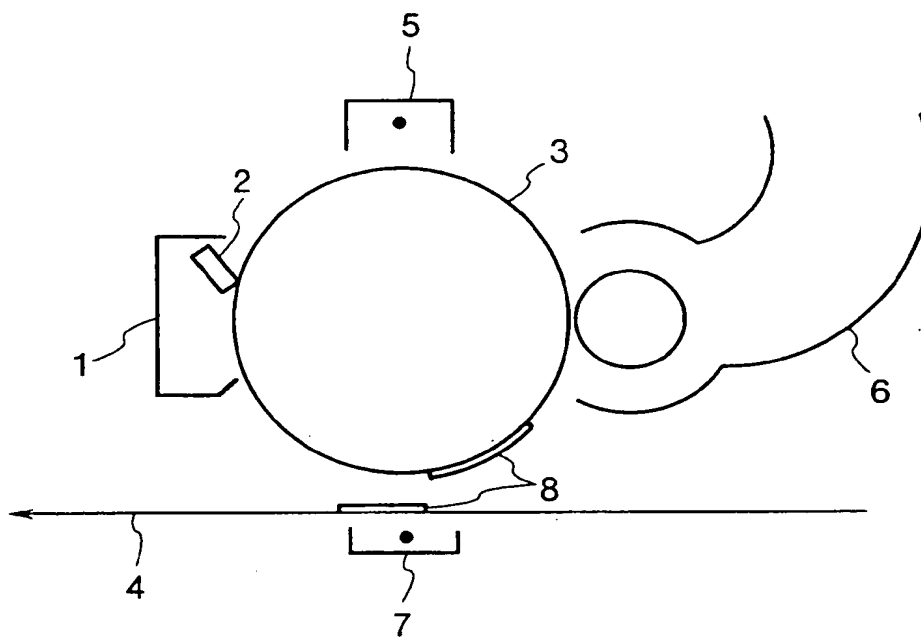
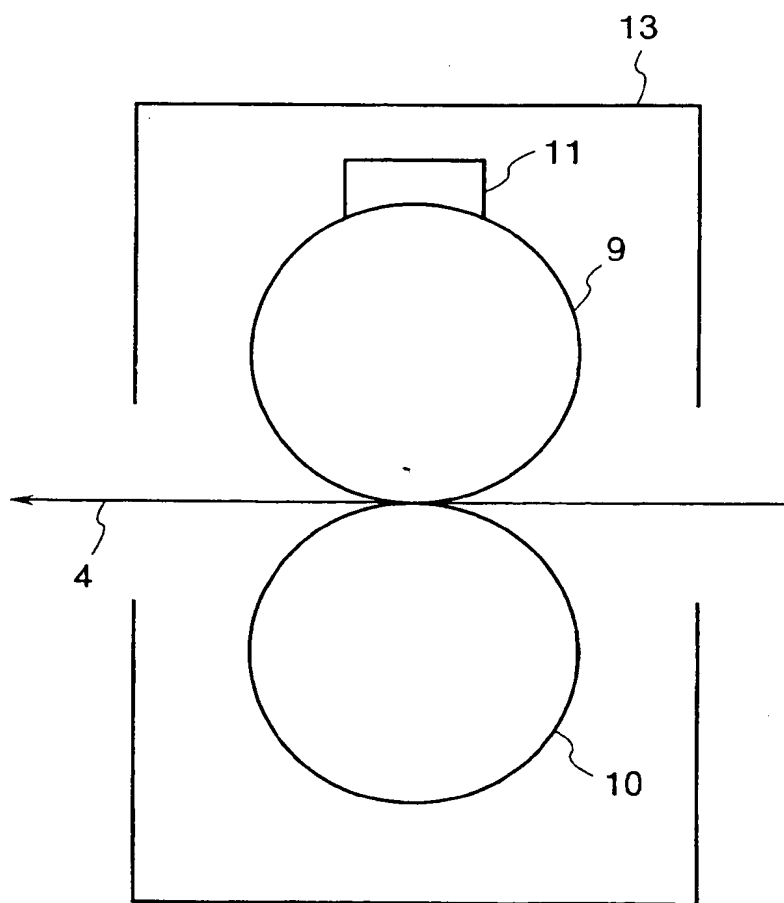


FIG.2







European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 94 11 7332

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	PATENT ABSTRACTS OF JAPAN vol. 10, no. 242 (M-509) (2298) 21 August 1986 & JP-A-61 072 581 (CANON) 14 April 1986 * abstract *	1-3,5	
A	US-A-4 576 867 (MIYAMOTO) * column 5; example 1 *	1-3,5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 3 March 1995	Examiner Vogt, C
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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